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DESCRIPTION

BLOCK COPOLYMER COMPOSITION

5   TECHNICAL FIELD

The present invention relates to a block copolymer
composition comprising a vinyl aromatic hydrocarbon and a
conjugated diene, particularly to a block copolymer
composition excellent in transparency and impact

10   resistance and useful as a block copolymer composition as
it is or useful for blending with various thermoplastic
resins.

BACKGROUND ART

15   A block copolymer comprising a vinyl aromatic
hydrocarbon and a conjugated diene, which has a
relatively high vinyl aromatic hydrocarbon content, has
been widely used for injection molding or extrusion
molding of a sheet, a film or the like by utilizing

20   properties such as transparency or impact resistance.

Particularly, some proposals have been made with
regard to a block copolymer and a styrenic polymer
composition having a block copolymer blended. The
proposed examples include a branched block copolymer of

25   two linear copolymers before coupling, which comprises
vinyl-substituted aromatic hydrocarbon blocks of a high
molecular weight content and a low molecular weight

content at a number average molecular ratio of from 3 to 7, and its production method (as illustrated in JP-A-53-000286) and a branched block copolymer comprising polymer blocks of at least 3 monomer units of vinyl aromatic hydrocarbons and its production method (as illustrated in JP-A-07-173232).

Further, there have been proposed a linear copolymer composition having a vinyl aromatic hydrocarbon block portion molecular weight distribution of from 2.3 to 4.5 or a branched block copolymer composition having a vinyl aromatic hydrocarbon block portion molecular weight distribution of from 2.8 to 3.5 which is prepared by blending (as illustrated in JP-A-52-078260), or a method of combining branched block copolymers having a vinyl aromatic hydrocarbon block portion molecular weight distribution outside the range of from 2.8 to 3.5 (as illustrated in JP-A-57-028150).

However, according to these methods, these block copolymers and compositions prepared by blending these block copolymers with various thermoplastic resins had a poor balance in respect of transparency and impact resistance, and a molded product prepared by injection molding under high shearing condition tends to easily generate anisotropic properties and the molded product thus prepared was unsatisfactory because strength became weak in one respect.

DISCLOSURE OF THE INVENTION

Under these circumstances, the present inventors have variously studied to obtain a block copolymer composition excellent in balance between transparency and impact resistance with regard to not only an extrusion-molded product and a blow-molded product but also an injection-molded product, and have discovered that not only an extrusion-molded product and a blow-molded product but also an injection-molded product of a block copolymer prepared by coupling reaction, which comprises a hard segment block made mainly of a vinyl aromatic hydrocarbon and a soft segment block made mainly of a conjugated diene, provided a remarkably improved impact resistance without degrading transparency by blending two kinds of block copolymers having a specific structure of hard segment block portion. The present invention has been accomplished on the basis of this discovery.

Thus, the present invention relates to a block copolymer composition which is a block copolymer composition comprising, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene, characterized in that it contains the following components A and B in a blend ratio within a range of component A/component B = 20 to 80/80 to 20 (mass ratio):

Component A is a block copolymer

(1) which comprises, as monomer units, from 55 to 95

mass% of a vinyl aromatic hydrocarbon and from 5 to 45

mass% of a conjugated diene,

(2) which is constituted by a hard segment block made

mainly of the vinyl aromatic hydrocarbon and a soft

5   segment block made mainly of the conjugated diene,

(3) wherein the hard segment block comprises blocks S1

and S2 made mainly of a vinyl aromatic hydrocarbon having

two types of different molecular weights, and when the

number average molecular weights of S1 and S2 are

10   represented by M1 and M2, respectively, M1 is within a

range of from 75,000 to 170,000 and M2 is within a range

of from 14,000 to 30,000, and their ratio M1/M2 is within

a range of from 4 to 9, and the ratio of S1 to S2 is

within a range of S1/S2 = 6 to 35/65 to 94 (molar ratio),

15   and

(4) which is produced by a coupling reaction; and

        component B is a block copolymer

(1) which comprises, as monomer units, from 55 to 95

mass% of a vinyl aromatic hydrocarbon and from 5 to 45

20   mass% of a conjugated diene,

(2) which is constituted by a hard segment block made

mainly of the vinyl aromatic hydrocarbon and a soft

segment block made mainly of the conjugated diene,

(3) wherein the hard segment block comprises blocks S3

25   and S4 made mainly of a vinyl aromatic hydrocarbon having

two types of different molecular weights, and when the

number average molecular weights of S3 and S4 are

represented by M3 and M4, respectively, M3 is within a

range of from 80,000 to 160,000 and M4 is within a range

of from 4,000 to 12,000 and their ratio M3/M4 is within a

range of from 13 to 22, and the ratio of S3 to S4 is

5   within a range of S3/S4 = 5 to 30/70 to 95 (molar ratio),

and

(4) which is produced by a coupling reaction.

EFFECTS OF THE INVENTION

10   The block copolymer composition obtained in the

present invention, which is a block copolymer as it is,

or a resin composition prepared by blending the block

copolymer with various thermoplastic resins, is

applicable to extrusion molding, blow molding, injection

15   molding, and other various molding processes, and can

produce molded products having a quite satisfactory

balance in respect of transparency and impact resistance.

The mechanism that the block copolymer composition

of the present invention produces a molded product having

20   such satisfactory transparency and impact resistance, is

not clear, but it is estimated to be as described below.

That is, the block copolymer composition of the present

invention, in its primary molecular structure, has an

average molecular weight, a molecular weight distribution

25   and a composition distribution in such effective ranges

as to achieve the above-mentioned properties, and its

obtained molded product has a regular microphase

separation structure and does not produce a macrolayer separation structure (when components in the composition form many macrophase separation structures of about at least 1 μm, visible light is dispersed and transparency

5 is lowered), and a soft segment in the microphase separation structure thus formed has a relatively high continuation.

BRIEF DESCRIPTION OF THE DRAWINGS

10 Fig. 1 illustrates a methine proton derived from an epoxy group present in an epoxidized oil residual group (proton having ● mark in Fig. 1).

Fig. 2 illustrates a methine proton derived from a ring opened epoxy group residue present in an epoxidized

15 oil residual group (proton having ◎ mark in Fig. 2).

BEST MODE FOR CARRYING OUT THE INVENTION

Examples of a vinyl aromatic hydrocarbon used in the block copolymer composition of the present invention

20 include styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene, α-methylstyrene, vinylnaphthalene, vinylanthracene or the like, and generally styrene. They may be used respectively alone or in a mixture of two or more.

25 Also, examples of a conjugated diene include a diolefin having one pair of conjugated double bonds and having a carbon number of from 4 to 8, such as 1,3-

butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene or the like, and generally 1,3-butadiene or isoprene. They may be used respectively alone or in a mixture of two or
5   more.

The block copolymer composition of the present invention comprises, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene, based on the total mass
10   amount of the copolymer composition.

When the block copolymer composition comprises, as monomer units, more than 95 mass% of a vinyl aromatic hydrocarbon and less than 5 mass% of a conjugated diene, the impact resistance of the block copolymer composition
15   becomes unpreferably low. On the other hand, when the block copolymer composition comprises, as monomer units, less than 55 mass% of a vinyl aromatic hydrocarbon and more than 45 mass% of a conjugated diene, the block copolymer composition provides unpreferable properties in
20   respect of transparency, moldability, stiffness, thermostability and the like.

When the block copolymer composition comprises, as monomer units, from 60 to 85 mass% of a vinyl aromatic hydrocarbon and from 15 to 40 mass% of a conjugated
25   diene, the block copolymer composition thus obtained provides more satisfactory balance in respect of impact resistance and transparency, and further when the block

copolymer composition comprises, as monomer units, from 65 to 80 mass% of a vinyl aromatic hydrocarbon and from 20 to 35 mass% of a conjugated diene, the block copolymer composition thus obtained provides much more satisfactory good balance in respect of impact resistance, transparency, moldability and the like.

The block copolymer composition of the present invention contains components A and B in a blend ratio within a range of component A/component B = 20 to 80/80 to 20 (mass ratio).

The component A is a block copolymer (1) which comprises, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene, (2) which is constituted by a hard segment block made mainly of the vinyl aromatic hydrocarbon and a soft segment block made mainly of the conjugated diene, (3) wherein the hard segment block comprises blocks S1 and S2 made mainly of a vinyl aromatic hydrocarbon having two types of different molecular weights, and when the number average molecular weights of S1 and S2 are represented by M1 and M2, respectively, M1 is within a range of from 75,000 to 170,000 and M2 is within a range of from 14,000 to 30,000, and their ratio of M1/M2 is within a range of from 4 to 9, and the ratio of S1 to S2 is within a S1/S2 = 6 to 35/65 to 94 (molar ratio), and (4) which is produced by a coupling reaction.

On the other hand, the component B is a block copolymer (1) which comprises, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene, (2) which is constituted by a hard segment block made mainly of the vinyl aromatic hydrocarbon and a soft segment block made mainly of the conjugated diene, (3) wherein the hard segment block comprises blocks S3 and S4 made mainly of a vinyl aromatic hydrocarbon having two types of different molecular weights, and when the number average molecular weights of S3 and S4 are represented by M3 and M4, respectively, M3 is within a range of from 80,000 to 160,000 and M4 is within a range of from 4,000 to 12,000 and their ratio M3/M4 is within a range of from 13 to 22, and the ratio of S3 to S4 is within a range of S3/S4 = 5 to 30/70 to 95 (molar ratio), and (4) which is produced by a coupling reaction.

When the component A comprises, as monomer units, more than 95 mass% of a vinyl aromatic hydrocarbon and less than 5 mass% of a conjugated diene, the impact resistance of the block copolymer composition finally obtained becomes unpreferably poor. On the other hand, when the component A comprises, as monomer units, less than 55 mass% of a vinyl aromatic hydrocarbon and more than 45 mass% of a conjugated diene, the block copolymer composition finally obtained provides unpreferably poor properties in respect of transparency, moldability,

stiffness, thermostability and the like. On the
contrary, when the component A comprises, as monomer
units, from 60 to 90 mass% of a vinyl aromatic
hydrocarbon and from 10 to 40 mass% of a conjugated
diene, the block copolymer composition finally obtained
provides a more satisfactory good balance in respect of
impact resistance and transparency, and when the
component A comprises, as monomer units, from 65 6o 85
mass% of a vinyl aromatic hydrocarbon and from 15 to 35
mass% of a conjugated diene, the block copolymer
composition finally obtained provides a much more
satisfactory good balance in respect of impact
resistance, transparency, moldability and the like.

Also, the component A is constituted by a hard
segment block made mainly of the vinyl aromatic
hydrocarbon and a soft segment block made mainly of the
conjugated diene.

The hard segment block made mainly of the vinyl
aromatic hydrocarbon means a block comprises, as monomer
units, from 70 to 100 mass% of a vinyl aromatic
hydrocarbon and from 0 to 30 mass% of a conjugated diene.
When the block made mainly of the vinyl aromatic
hydrocarbon is a block comprising, as monomer units, from
80 to 100 mass% of a vinyl aromatic hydrocarbon and from
0 to 20 mass% of a conjugated diene, the block copolymer
composition finally obtained preferably has a
satisfactory stiffness, and a block comprising, as

monomer units, from 95 to 100 mass% of a vinyl aromatic hydrocarbon and from 0 to 5 mass% of a conjugated diene is more preferable, and a block comprising, as monomer units, a vinyl aromatic hydrocarbon is further

5   preferable.

Also, when the block made mainly of a vinyl aromatic hydrocarbon is a copolymer block comprising, as monomer units, a vinyl aromatic hydrocarbon and a conjugated diene, the arrangement system of the monomer units may be

10   a random structure or a taper structure, or also may be a block structure. Examples of the block structure includes a structure represented by V-D-V (the polymerization degree of V on the both sides of D may be the same or different) wherein D represents a conjugated

15   diene block and V represents a vinyl aromatic hydrocarbon block.

Also, the soft segment block made mainly of a conjugated diene means a block comprising monomer units, from 60 to 100 mass% of a conjugated diene and from 0 to

20   40 mass% of a vinyl aromatic hydrocarbon. When the block made mainly of a conjugated diene is a block comprising, monomer units, from 70 to 100 mass% of a conjugated diene and from 0 to 30 mass% of a vinyl aromatic hydrocarbon, the block copolymer thus obtained has preferably a

25   satisfactory impact resistance, and a block comprising a conjugated diene as monomer units is more preferable. When a copolymer block comprising a conjugated diene and

a vinyl aromatic hydrocarbon is used as the soft segment block, the arrangement system of monomers may be any of a taper structure and a random structure, but a random structure is preferable.

Further, the hard segment block in component A comprises blocks S1 and S2 made mainly of a vinyl aromatic hydrocarbon having two types of different molecular weights, and when the number average molecular weight of S1 and S2 are represented by M1 and M2, respectively, M1 is within a range of from 75,000 to 170,000 and M2 is within a range of from 14,000 to 30,000, and their ratio M1/M2 is within a range of from 4 to 9, and the ratio of S1 to S2 is within a range of S1/S2 = 6 to 35/65 to 94 (molar ratio).

When the hard segment block in component A comprises blocks made mainly of a vinyl aromatic hydrocarbon having two types of different molecular weights, the finally obtained block copolymer composition provides a satisfactory molding processability and also provides a good balance in respect of transparency and impact resistance.

Also, when the blocks made mainly of two types of vinyl aromatic hydrocarbons are represented by S1 and S2, it is essential for the component A that the number average molecular weight M1 is within a range of from 75,000 to 170,000 and the number average molecular weight M2 is within a range of from 14,000 to 30,000. If the

number average molecular weight M1 of S1 is less than

75,000, the finally obtainable block copolymer

composition becomes poor in respect of impact resistance,

and if it exceeds 170,000, the transparency of the

5   finally obtained block copolymer composition is lowered.

If the number average molecular weight M2 of S2 is

less than 14,000, the finally obtainable block copolymer

composition becomes poor in respect of transparency and

impact resistance, and if it exceeds 30,000, the impact

10   resistance of the finally obtainable block copolymer

composition is lowered. In view of good molding

processability and well balanced transparency and impact

resistance of the finally obtainable block copolymer

composition, particularly preferable number average

15   molecular weight ranges of S1 and S2 are respectively a

range of from 100,000 to 150,000 and a range of from

15,000 to 18,000.

Further, the ratio M1/M2 of number average molecular

weights M1 and M2 of component A is within a range of

20   from 4 to 9. If the ratio M1/M2 is less than 4, the

finally obtainable block copolymer composition becomes

poor in respect of molding processability and impact

resistance, and if the ratio M1/M2 exceeds 9, the

transparency of the finally obtained block copolymer

25   composition becomes poor. In view of good molding

processability and well balanced transparency and impact

resistance of the finally obtainable block copolymer

composition, a particularly preferable range of the M1/M2 ratio is a range of from 5 to 8.

Also, in component A, the ratio of the two types of blocks is fixed in such a manner as to provide the ratio of S1 to S2 in a range of S1/S2 = 6 to 35/65 to 94 (molar ratio). In this manner, the finally obtainable block copolymer composition provides good molding processability and well balanced transparency and impact resistance. If the ratio of S1 is lower than the lower limit of the above range and the ratio of S2 is higher than the higher limit of the above range, the block copolymer becomes poor in respect of impact resistance and transparency, and if the ratio of S1 is higher than the higher limit of the above range and if the ratio of S2 is lower than the lower limit of the above range, the block copolymer provides poor processability and also provides poor impact resistance. In view of good molding processability and well balanced transparency and impact resistance of the block copolymer, a particularly preferable ratio of S1 and S2 is within a ratio of S1/S2 = 10 to 30/70 to 90 (molar ratio).

The molecular weight of component A is not particularly limited, but in view of molding processability of the block copolymer composition of the present invention, a preferable molecular weight range is from 60,000 to 160,000 as a number average molecular weight and from 90,000 to 220,000 as a weight average

molecular weight. A more preferable range is from 80,000 to 140,000 as a number average molecular weight and from 120,000 to 200,000 as a weight average molecular weight. Also, the molecular weight distribution of component A is

5   not specially limited, but in view of molding processability of the block copolymer composition of the present invention, a preferable molecular weight distribution (weight average molecular weight/number average molecular weight) range is from 1.2 to 1.8, more

10 preferably from 1.3 to 1.6.

Also, component A is a block copolymer produced by a coupling reaction. Component A is produced by general living anion polymerization method using an organic lithium compound as an initiator in a hydrocarbon

15 solvent. Monomers of a vinyl aromatic hydrocarbon and a conjugated diene are subjected to anion polymerization using an organic lithium compound as an initiator in a hydrocarbon solvent to form a living active terminal, and the living active terminal is then reacted with a

20 coupling agent added to carry out coupling reaction for synthesis. Thus, the coupling reaction couples polymer chains having living active sites at one terminal and bond them. The coupling agent is a compound having at least two reactive sites per molecule capable of

25 attacking living active sites and coupling and bonding polymer chains having living active sites at one side of terminals.

The coupling agent used in the present invention may be a difunctional coupling agent having two reactive sites per molecule or may be a polyfunctional coupling agent having at least three reactive sites per molecule. Only one kind of polyfunctional coupling agent may be used, or at least two kinds of polyfunctional coupling agents may be used, or further at least one kind of difunctional coupling agent and at least one kind of polyfunctional coupling agent may be used in combination. Preferably, only one kind of polyfunctional coupling agent is used.

When carrying out the coupling reaction, the reactive sites of the coupling agent attacked by living active sites are not necessarily completely reacted, but a part of the reactive sites may remain unreacted. Further, all of polymer chains having living active sites at one side of terminals are not always completely reacted with all of the reactive sites of the coupling agent, but unreacted polymer chains may remain in the block copolymer finally obtained.

Also, by using a polyfunctional coupling agent, a block copolymer having a branch number smaller than a branch number estimated to be completely reacted with the reactive sites of the coupling agent may coexist in the finally produced block copolymer, or a polymer chain having its living active sites simply replaced by a coupling agent or a polymer chain having one side

terminal bonded with a coupling chain only may coexist in the finally produced block copolymer.

In such a case, component A obtained by using a difunctional coupling agent, includes a mixture of a block copolymer having the reactive sites of the coupling agent completely reacted, a polymer chain having a living active site replaced simply by the coupling agent and a polymer chain remained without reacting with the reactive site of the coupling agent. Also, component A obtained by using a polyfunctional coupling agent, includes a mixture of at least two of a block copolymer having a branch number equivalent to a branch number estimated to be completely reacted with the reactive sites of the coupling agent, a block copolymer having a branch number smaller than a branch number estimated to be completely reacted with the reactive sites of the coupling agent, a polymer chain having a living active site replaced and bonded simply by the coupling agent and a polymer chain remaining without reacting with the reactive sites of the coupling agent.

Examples of the coupling agent used in the present invention include a chlorosilane type compound such as silicon tetrachloride, 1,2-bis(methyldichlorosilyl)ethane or the like, an alkoxysilane type compound such as tetramethoxysilane, tetraphenoxysilane or the like, tin tetrachloride, a polyhalogenated hydrocarbon, a carboxylic acid ester, a polyvinyl compound, and an

epoxidized oil such as epoxidized soybean oil, epoxidized linseed oil or the like.

Among these coupling agents, examples of a difunctional coupling agent having two reactive sites per molecule, include dimethyldichlorosilane, dimethyldimethoxysilane and the like. Examples of a polyfunctional coupling agent having at least 3 reactive sites per molecule include methyltrichlorosilane, methyltrimethoxysilane, tetrachlorosilane, tetramethoxysilane, tetraphenoxysilane and the like. Also, an epoxidized oil is a polyfunctional coupling agent since it has carbonyl carbons of 3 ester bonds per molecule and has a long chain alkyl group having at least one epoxy group.

A coupling agent preferably usable in the present invention is a polyfunctional coupling agent, and among them, an epoxidized oil is preferable. Examples of the epoxidized oil include epoxidized soybean oil, epoxidized linseed oil or the like, and among them, epoxidized soybean oil is particularly preferable.

Such an epoxidized oil as epoxidized soybean oil or epoxidized linseed oil is a compound of an epoxidized glycerin ester of a mixture of long chain carboxylic acids including an unsaturated acid such as oleic acid, linolic acid, linolenic acid or the like. When these compounds are used as a polyfunctional coupling agent, branch numbers of block copolymers obtained are

respectively 5, 3 and 4, corresponding to their structures of one linolenic acid residue having three epoxy groups and one carbonyl group, one oleic acid residue having one epoxy group and one carbonyl group, and one linolic acid residue having two epoxy groups and one carbonyl group. Thus, when all of their reactive sites are completely reacted, block copolymer compositions having branch numbers respectively of 3 to 5 are obtained, and the maximum branch number among them is 5.

Also, component B is the same as component A in respect that it is a block copolymer (1) which comprises, as monomer units, from 55 to 95 mass% of a vinyl aromatic hydrocarbon and from 5 to 45 mass% of a conjugated diene, (2) which is constituted by a hard segment block made mainly of the vinyl aromatic hydrocarbon and a soft segment block made mainly of the conjugated diene, and (4) which is produced by a coupling reaction, and such requirements as defined with regard to component A are applicable also to component B.

However, component B is different from component A in respect of (3) wherein the hard segment block comprises blocks S3 and S4 made mainly of two kinds of vinyl aromatic hydrocarbons having different molecular weights, and when the number average molecular weight of S3 and S4 are represented by M3 and M4, respectively, M3 is within a range of from 80,000 to 160,000 and M4 is

within a range of from 4,000 to 12,000 and their ratio M3/M4 is within a range of from 13 to 22, and the ratio of S3 to S4 is within a range of S3/S4 = 5 to 30/70 to 95 (molar ratio). This different point is described hereinafter.

The hard segment block of component B is a block made mainly of a vinyl aromatic hydrocarbon having two types of different molecular weights. Accordingly, the finally obtainable block copolymer composition provides good molding processability and well balanced transparency and impact resistance, and this point is the same as component A.

However, in component B, it is essential that blocks S3 and S4 made mainly of two types of vinyl aromatic hydrocarbons respectively have number average molecular weights M3 and M4 respectively of a range of from 80,000 to 160,000 and a range of from 4,000 to 12,000. If the number average molecular weight M3 of S3 is less than 80,000, the finally obtainable block copolymer composition is poor in respect of impact resistance, and if it exceeds 160,000, the finally obtainable block copolymer composition is poor in respect of not only impact resistance but also transparency. If the number average molecular weight M4 of S4 is less than 4,000, the finally obtainable block copolymer composition becomes poor in respect of transparency and also poor in respect of molding processability because its fluidity becomes

too high. On the other hand, if it exceeds 12,000, the finally obtainable block copolymer composition provides a lower impact resistance. In view of well balanced good molding processability, transparency and impact

5   resistance of the finally obtainable block copolymer composition, M3 is preferably from 90,000 to 140,000, and M4 is preferably from 4,000 to 12,000, more preferably from 5,000 to 9,000.

Further, in component B, it is essential that the

10   number average molecular weights M3 and M4 should have a ratio of M3/M4 in a range of from 13 to 22. If the ratio M3/M4 is less than 13, the finally obtainable block copolymer composition becomes poor in respect of impact resistance, and if the ratio M3/M4 exceeds 22, the

15   finally obtainable block copolymer composition becomes poor in respect of transparency. In view of well balanced good molding processability, transparency and impact resistance of the finally obtained block copolymer composition, a particularly preferable M1/M2 ratio is in

20   a range of from 14 to 19.

Also, in component B, a ratio of two types of blocks S3 and S4 is fixed in such a manner as to provide a range of S3/S4 = 5 to 30/70 to 95 (molar ratio). In this manner, the finally obtained block copolymer composition

25   provides well balanced good molding processability, transparency and impact resistance. If the proportion of S3 is lower than the lower limit of the above range and

if the proportion of S4 is higher than the upper limit of the above range, the block copolymer composition becomes poor in respect of impact resistance and transparency, and if the proportion of S3 exceeds the upper limit of the above range and the proportion of S4 is lower than the lower limit of the above range, the block copolymer composition becomes poor also in respect of impact resistance, and molding processability becomes low. In view of well balanced good molding processability, transparency and impact resistance of the block copolymer, a particularly preferable ratio of S3 and S4 is S3/S4 = 10 to 25/75 to 90 (molar ratio).

Also, the molecular weight of component B is not specially limited, but in view of molding processability of the block copolymer composition of the present invention, a preferable molecular weight range is from 60,000 to 110,000 as a number average molecular weight and from 100,000 to 180,000 as a weight average molecular weight. A more preferable range is from 80,000 to 90,000 as a number average molecular weight and from 120,000 to 150,000 as a weight average molecular weight. Also, the molecular weight distribution of component B is not particularly limited, but in view of molding processability of the block copolymer composition of the present invention, a preferable molecular weight distribution range is from 1.3 to 2.0, more preferably from 1.4 to 1.8.

The block copolymer composition of the present invention contains these components A and B in a mixing ratio of component A/component B = 20 to 80/80 to 20 (mass ratio). When the mixing ratio is within this range, a block copolymer composition having well balanced good molding processability, impact resistance and transparency is obtainable.

If the mixing proportion of component A is less than 20 and the mixing proportion of component B exceeds 80, the finally obtainable block copolymer composition becomes poor in respect of molding processability because its fluidity becomes too high, and also becomes poor in respect of transparency. On the other hand, if the mixing proportion of component A exceeds 80 and the mixing proportion of component B is less than 20, the finally obtainable block copolymer composition becomes poor in respect of molding processability because its fluidity is lowered, and also becomes poor in respect of impact strength.

Particularly, a block copolymer comprising component A alone provides a remarkably low fluidity and a very poor impact strength, and a block copolymer comprising component B alone provides a remarkably high fluidity and a very poor transparency, but such a block copolymer composition comprising a mixture of component A and component B as in the present invention provides well balanced good molding processability, impact resistance

and transparency.

Further, a more preferable mixing ratio is component A/component B = 30 to 70/70 to 30 (mass ratio).

A molecular weight of a block copolymer composition

5   containing component A and component B of the present invention is not specially limited, but in view of molding processability of the block copolymer composition, a preferable molecular weight range is from 60,000 to 140,000 as a number average molecular weight

10 and from 110,000 to 200,000 as a weight average molecular weight. A more preferable range is from 80,000 to 110,000 as a number average molecular weight and from 120,000 to 180,000 as a weight average molecular weight. Also, a molecular weight distribution of the block

15 copolymer composition is not specially limited, but in view of molding processability of the block copolymer composition, a preferable molecular weight distribution range is from 1.4 to 2.0, more preferably from 1.4 to 1.8.

20 As mentioned above, component A and component B in the present invention are obtainable by general living anion polymerization method using an organic lithium compound as an initiator in a hydrocarbon solvent. Thus, monomers of a vinyl aromatic hydrocarbon and a conjugated

25 diene are subjected to anion polymerization using an organic lithium compound as an initiator in a hydrocarbon solvent to form living active terminals, and the living

active terminals are then reacted with a coupling agent added by coupling method. For example, when producing component A and component B comprising a block of monomers of a vinyl aromatic hydrocarbon as a hard segment block and a block of monomers of a conjugated diene as a soft segment block, a vinyl aromatic hydrocarbon is anion-polymerized in the presence of an initiator, and then the initiator and a vinyl aromatic hydrocarbon are successively added to the polymerization system to form a polymer block comprising monomer units of two types of vinyl aromatic hydrocarbons having different molecular weights, and a conjugated diene is then added thereto, finally followed by coupling step.

Examples of the organic solvent used for producing component A and component B include an aliphatic hydrocarbon such as butane, pentane, hexane, isopentane, heptane, octane, isooctane or the like, a cycloaliphatic hydrocarbon such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, ethylcyclohexane or the like, an aromatic hydrocarbon such as benzene, toluene, ethyl benzene, xylene or the like, and other well known organic solvents.

Also, the organic lithium compound is a compound having at least one lithium atom bonded in a molecule, such as ethyl lithium, n-propyl lithium, isopropyl lithium, n-butyl lithium, sec-butyl lithium, t-butyl lithium or the like.

In the production of component A and component B of
the present invention, a small amount of a polar compound
may be dissolved in a solvent. The polar compound is
used for improving efficiency of an initiator or for
5   adjusting microcomposition of a conjugated diene, or used
as a randomizing agent when copolymerizing a vinyl
aromatic hydrocarbon and a conjugated diene. Examples of
the polar compound used for producing component A and
component B of the present invention include ethers such
10 as tetrahydrofuran, diethylene glycol dimethyl ether,
diethylene glycol dibutyl ether or the like, amines such
as triethylamine, tetramethylethylenediamine or the like,
thioethers, phosphines, phosphoramides, alkylbenzene
sulfonates, alkoxides of potassium or sodium, and the
15 like, and a preferable polar compound is tetrahydrofuran.

Polymerization temperature for preparing component A
and component B in the present invention is generally
from -10°C to 150°C, preferably from 40°C to 120°C.
Polymerization time varies depending on conditions, but
20 is generally within 48 hours, particularly preferably
from 0.5 to 10 hours. Also, atmosphere for
polymerization system is preferably replaced by an inert
gas such as nitrogen gas. Polymerization pressure is not
specially limited, but may be such a pressure as to be
25 sufficient for maintaining monomers and solvents at a
liquid phase in the above polymerization temperature
range. Further, it is necessary to pay such attention

that the polymerization system is not contaminated with
impurities such as water, oxygen or carbonic acid gas
which may deactivate an initiator and a living polymer.

After finishing polymerization and coupling

5 reactions, an active block copolymer which does not
participate in the coupling reaction, is deactivated by
adding a material having active hydrogen such as water,
alcohol, carbon dioxide, an organic acid or an inorganic
acid as a polymerization terminator in an amount

10 sufficient to deactivate active terminals. At this time,
when using water or alcohols as a polymerization
terminator, hydrogen is introduced into polymerization
chain terminals, and when using carbon dioxide, a
carboxyl group is introduced into polymerization chain

15 terminals. Accordingly, by appropriately selecting a
polymerization terminator, it is possible to produce a
block copolymer containing a block copolymer component
having various functional groups at the terminals.

An amount of a coupling agent may be an optional

20 effective amount, but is preferably adjusted to such an
amount as to make the reactive sites of the coupling
agent stoichiometrically excessively present to the
living active terminals. For example, it is preferable
to add the coupling agent in such an amount as to make

25 the reactive sites present in an amount of 1 to 2
equivalents to mol number of living active terminals
present in a polymerization solution before coupling

step. In this manner, a mol number of lithium atom present in the reaction system can be calculated from a charged amount of an organic lithium compound, for example, as an initiator, and accordingly by considering this mol number as a mol number of the living active terminals, an amount of the coupling agent to be added in such an amount as to make a desired equivalent number of reactive sites present in the reaction system, can be determined. This equivalent amount is expressed by defining a reactive site number of a coupling agent added to the reaction system as a multiple number of living active terminal number.

In a case that the block copolymer composition of the present invention is a block copolymer composition containing component A and component B prepared by coupling using an epoxidized oil, when a proportion of a mol number of ring-opened epoxy group residues present in the epoxidized oil residues in the block copolymer composition is less than 0.7 to a total mol number of the ring-opened epoxy residues and epoxy groups present in the epoxidized oil residues, a mixture resin composition of the block copolymer composition and a styrene type resin is improved in respect of impact resistance and provides a preferable good balance of transparency, molding processability and other physical properties. The proportion of the above mol number is more preferably from 0.03 to 0.65, most preferably from 0.03 to 0.5.

particularly, when this proportion is within a range of
from 0.1 to 0.3, the block copolymer composition provides
an improved impact resistance, particularly such an
impact resistance in the presence of a notch as

5   represented by Charpy impact strength. This proportion
can be controlled by an amount of a coupling agent to be
added in the coupling step, and the amount of the
coupling agent is adjusted in such an amount as to make
the reactive sites present preferably in an amount of 1

10   to 2 equivalents, more preferably from 1 to 1.5
equivalents, in the reaction system.

The proportion to the above mol number can be
determined by proton NMR spectrum measurement of the
block copolymer composition of the present invention by

15   using a deuterium substituted solvent such as deuterium
substituted chloroform, deuterium substituted
tetrahydrofuran or the like or carbon tetrachloride.

In order to adjust the proportion of mol number of
ring-opened epoxy group residues present in an epoxidized

20   oil residue in the block copolymer composition of the
present invention less than 0.7 to the total mol number
of the ring-opened epoxy group residues and epoxy groups
present in the epoxidized oil residue, it is preferable
for achieving a good balance of impact resistance,

25   transparency, molding processability and other physical
properties of a mixture resin composition of the block
copolymer composition and a styrenic resin to control the

proportion of mol number of each of component A and component B of the block copolymer composition respectively less than 0.7 to the total mol number of the ring-opened epoxy group residues and epoxy groups present in the epoxidized residue.

Hereinafter, a particularly preferable structure of each of component A and component B constituting the block copolymer composition of the present invention is illustrated below.

Component A is a block copolymer having a block made mainly of a vinyl aromatic hydrocarbon having two types of different molecular weights produced by coupling reaction, examples of which include a mixture of three types of block copolymers as defined in the following (1).

S1-B1, S2-B1, (S1-B1)i-X-(B1-S2)m (1)

(wherein each of S1 and S2 represents a hard segment block made mainly of a vinyl aromatic hydrocarbon, B1 represents a soft segment block made mainly of a conjugated diene, the number average molecular weight of B1 is within a range of from 10,000 to 30,000, X is a residual group of a coupling agent, each of i and m is an integer of 0 or more, and i+m is at least 1 and at most 8.)

In component A, the molecular weight of block B1 made mainly of a conjugated diene as a soft segment block is preferably in a range of from 10,000 to 30,000 as a

number average molecular weight. If the molecular weight
is within this range, a block copolymer having a good
balance in transparency, impact resistance and molding
processability can be obtained. If the soft segment

5 block B1 has a number average molecular weight of less
than 10,000, the block copolymer becomes poor in respect
of impact resistance, and if the number average molecular
weight exceeds 30,000, the block copolymer becomes poor
in respect of transparency and molding processability.

10 In order to obtain a block copolymer having a good
balance in transparency, impact resistance and molding
processability, the number average molecular weight of
the soft segment block is particularly preferably in a
range of from 11,000 to 26,000. Also, if i+m is at least

15 1 and at least 8, a block copolymer having satisfactory
transparency, impact resistance and molding
processability can be obtained, and i+m is more
preferably at least 1 and at most 5.

It is preferable that component A contains a

20 branched block copolymer in an amount of from 65 to 90
mass%. The branched block copolymer is a component that
a remaining polymer chain which does not participate in
coupling reaction and a polymer chain having a living
active site simply replaced and bonded with a coupling

25 chain, are removed from the block copolymer mixture as
defined in (1).

The content of the branched block copolymer in

component A can be determined by gel permeation chromatogram in the following manner.

That is, in the gel permeation chromatogram of component A, a peak area of a branched block copolymer in component A is determined by calculating a sum of peak areas corresponding to linear block copolymers S1-B1 and S2-B1 before coupling (this is a sum of peak areas of a remaining polymer chain which does not participate in coupling reaction and a polymer chain having a living active site simply replaced and bonded with a coupling agent) and deducting this value from a total peak area value.

By expressing the above determined peak area of a branched block copolymer to the total peak area by percentage, the branched block copolymer content in component A can be determined as mass%.

A particularly preferable branched block copolymer content is in a range of from 70 to 85 mass%. If the branched block copolymer content in component A is less than 65 mass%, a mixture resin composition of the block copolymer and a styrenic resin becomes poor in respect of impact resistance, transparency and molding processability, and if the content exceeds 90 mass%, a mixture resin composition of the block copolymer and a styrenic resin provides a poor impact resistance.

Next, component B contains a block copolymer having a block made mainly of a vinyl aromatic hydrocarbon

having two types of different molecular weights produced
by coupling reaction, examples of which include a mixture
of three types of block copolymers as defined in the
following (2).

5        $S3-B2$, $S4-B2$, $(S3-B2)n-Y-(B2-S4)o$ (2)
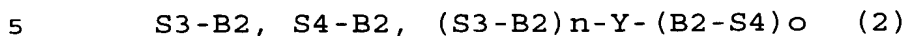
(wherein each of S3 and S4 is a hard segment block made
mainly of a vinyl aromatic hydrocarbon, B2 represents a
soft segment block made mainly of a conjugated diene, the
number average molecular weight of B2 is within a range

10   of from 9,000 to 20,000, Y is a residual group of a
coupling agent, each of n and o is an integer of 0 or
more, and n+o is at least 1 and at most 8.)

In component B, the molecular weight of the block B2
made mainly of a conjugated diene as a soft segment block

15   is preferably in a range of 9,000 to 20,000 as a number
average molecular weight. If the molecular weight is
within this range, it is possible to obtain a block
copolymer having a good balance in transparency, impact
resistance and molding processability. If the number

20   average molecular weight of the soft segment block B2 is
less than 9,000, the block copolymer provides a poor
impact resistance, and if the molecular weight exceeds
20,000, transparency and molding property become poor.
In order to obtain a block copolymer having a good

25   balance in transparency, impact resistance and molding
processability, a particularly preferable number average
molecular weight range of the soft segment block is from

12,000 to 16,000. Also, if n+o is at least 1 and at most

8, a block copolymer having satisfactory transparency,

impact resistance and molding processability can be

obtained, and n+o is more preferably at least 1 and at

5   most 5.

It is preferable that component B contains a

branched block copolymer in an amount of from 65 to 90

mass%. The branched block copolymer is a component that

a remaining polymer chain which does not participate in

10   coupling reaction and a polymer chain having a living

active site simply replaced and bonded with a coupling

agent are removed from a block copolymer mixture as

defined in (2). The content of the branched block

copolymer in component B can be determined by gel

15   permeation chromatogram in the same manner as in

component A. A particularly preferable branched block

copolymer content in component B is within a range of

from 70 to 85 mass%. If the branched block copolymer

content in component B is less than 65 mass%, a mixed

20   resin composition of the block copolymer and a styrenic

resin becomes poor in respect of impact resistance,

transparency and molding processability, and if the

branched block copolymer content exceeds 90 mass%, a

mixed resin composition of the block copolymer and a

25   styrenic resin becomes poor in respect of impact

resistance.

The block copolymer composition of the present

invention is obtained by mixing component A and component B. A mixing method is not specially limited, and a deactivated solution after polymerizing component A and component B, may be mixed, or a mixture of pellets of

5 component A and component B may be melt-kneaded by an extruder.

If necessary, the block copolymer composition of the present invention may be blended with various additives. For example, additives such as a stabilizer, a lubricant,

10 a processing aid, an anti-blocking agent, an antistatic agent, an anti-clouding agent, a weather resistance-improving agent, a softening agent, a plasticizer, a pigment and the like may be blended in order to prevent physical properties from being degraded when the block

15 copolymer is subjected to various heat treatments or when its molded product is used in an oxidizing atmosphere or under irradiation with ultraviolet rays, or in order to further impart physical properties suitable for a use object.

20 Examples of the stabilizer include a phenol type antioxidant such as 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenylacrylate, 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenylacrylate, octadecyl-3-(3,5-di-tert-butyl-4-

25 hydroxyphenyl)propionate, 2,6-di-tert-butyl-4-methylphenol or the like, and a phosphorus type antioxidant such as 2,2-methylenebis(4,6-di-tert-

butylphenyl)octylphosphite, trisnonylphenylphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol-diphosphite or the like.

Also, examples of the lubricant, processing aid, anti-blocking agent, antistatic agent or anti-clouding agent include a saturated aliphatic acid such as palmitic acid, stearic acid, behenic acid or the like, an aliphatic acid ester such as octyl palmitate, octyl stearate or the like, a pentaerythritol aliphatic acid ester, an aliphatic acid amide such as erucic amide, oleic amide, stearic amide or the like, ethylenebis stearic amide, or glycerin-mono-aliphatic acid ester, glycerin-di-aliphatic acid ester, a sorbitan aliphatic acid ester such as sorbitan-mono-palmitic acid ester, sorbitan-mono-stearic acid ester or the like, a higher alcohol such as myristyl alcohol, cetyl alcohol, stearyl alcohol, or the like.

Examples of the weather resistance-improving agent include a benzotriazole type agent such as 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole or the like, a salicylate type agent such as 2,4-di-tert-butylphenyl-3',5'-di-tert-butyl-4'-hydroxybenzoate or the like, a benzophenone type UV ray absorber such as 2-hydroxy-4-n-octoxybenzophenone or the like, or a hindered amine type weather resistance-improving agent such as tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate or the like. Further, white oil,

silicone oil or the like may be added.

These additives are blended with the block copolymer composition of the present invention preferably in an amount of from 0 to 5 mass%.

5   The block copolymer composition thus obtained in the present invention can be easily molded into various practically useful products including sheets, foams, films, and other variously shaped injection molded products, blow molded products, pressure blow molded

10   products, vacuum molded products, biaxially oriented molded products, and the like by employing conventional well known optional molding methods such as extrusion molding, injection molding, blow molding or the like.

If necessary, the block copolymer composition of the

15   present invention may be blended with various thermoplastic resins to form resin compositions.

Examples of usable thermoplastic resins include a polystyrene type polymer, a polyphenylene ether type polymer, a polyethylene type polymer, a polypropylene

20   type polymer, a polybutene type polymer, a polyvinyl chloride type polymer, a polyvinyl acetate type polymer, a polyamide type polymer, a thermoplastic polyester type polymer, a polyacrylate type polymer, a polyphenoxy type polymer, a polyphenylene sulfide type polymer, a

25   polycarbonate type polymer, a polyacetal type polymer, a polybutadiene type polymer, a thermoplastic polyurethane type polymer, a polysulfine type polymer and the like,

but a preferable thermoplastic resin is a styrene type polymer, and among them, polystyrene resin, styrene-butyl acrylate copolymer and styrene-methyl methacrylate copolymer are particularly preferably usable.

5   A blending mass ratio of the block copolymer composition of the present invention and a thermoplastic resin is preferably block copolymer composition/thermoplastic resin = 3/97 to 90/10. If the blending amount of the block copolymer composition is

10   less than 3 mass%, impact resistance of the resin composition thus formed is not fully improved, and if the blending amount of the thermoplastic resin is less than 10 mass%, stiffness expected to be improved by being blended with the thermoplastic resin is not sufficient.

15   A particularly preferable blending mass ratio of the block copolymer composition and the thermoplastic resin is block copolymer composition/thermoplastic resin = 30/70 to 80/20, more preferably block copolymer composition/thermoplastic resin = 40/60 to 70/30.

20   Hereinafter, the present invention is illustrated with reference to Examples. However, the present invention is not limited to these Examples. The data shown in the Examples and Comparative Examples were measured in accordance with the following method.

25   Total light transmittance and cloud value were measured in accordance with JIS-K7105, and Charpy impact strength was measured in accordance with JIS K-7111

(having notch) by preparing a test piece molded from resin pellets by injection molding machine.

Dropping weight impact strength was measured by forming a flat plate having a thickness of 2 mm by injection molding machine, naturally dropping a weight of 6.5 kg from a height of 62 cm onto the flat face of the flat plate test piece fixed by a holder (diameter 40 mm) by using dropping weight graphic impact tester (trademark of instrumented dropping weight impact tester of Toyo Seiki Seisaku-Sho, Ltd.), having the test piece completely destroyed or penetrated by a striker (diameter 12.7 mm) fixed at the lower part of the weight, and measuring total energy (referred to as total absorption energy) required at this time.

Polybutadiene rubber component amount (PBd amount) in a block copolymer composition was determined by halogen addition method adding iodine chloride into a double bond.

Flow properties (MFR) under a high temperature was measured in accordance with JIS-K7210.

Measuring conditions of gel permeation chromatography (GPC) are illustrated in the following measuring condition 1 and measuring condition 2.

MEASURING CONDITION 1

Solvent (mobile phase): THF

Flow rate: 1.0 ml/min

Temperature: 40°C

Column structure: Three columns in total

(theoretical step number 32,000 steps in total) composed

of one column of TSK guard column MP (xL) 6.0 mmID x 4.0

cm manufactured by Tosoh Corporation and two columns of

5   TSK-GEL MULTIPORE HXL-M, 7.8 mmID x 30.0 cm (theoretical

step number 16,000 steps) manufactured by Tosoh

Corporation arranged in this order

Amount of sample charged: 100 µL (sample solution

concentration 1 mg/ml)

10   Pressure of charging solution: 39 kg/cm^2

Detector: RI detector

MEASURING CONDITION 2

Solvent (mobile phase): THF

Flow rate: 0.2 ml/min

15   Temperature: 40°C

Column structure: Five columns in total (theoretical

step number 100,000 steps in total) of one column of KF-G

4.6 mmID x 10 cm manufactured by Showa Denko K.K. and

four columns of KF-404HQ, 4.6 mmID x 250 cm manufactured

20   by Showa Denko K.K. (theoretical step number 25,000

steps) arranged in this order

Amount of sample charged: 10 µL (sample solution

concentration 2 mg/ml)

Pressure of charging solution: 127 kg/cm^2

25   Detector: RI detector

Number average molecular weight of a soft segment

block made mainly of a conjugated diene was measured in

the following manner. In the case of component A, when number average molecular weight values of respective peaks corresponding to GPC chromatogram under measuring condition 1 of a mixture of S1 and S2 are represented respectively by M1 and M2 and number average molecular weight values of respective peaks corresponding to GPC chromatogram under measuring condition 2 of a mixture of S1-B1 and S2-B1 are represented respectively by M5 and M6, value X obtained by the following formula is defined as a polystyrene conversion value of a number average molecular weight of a soft segment block.

$$X = \{ (M5 - M1) + (M6 - M2) \} / 2$$

Thereafter, a standard polybutadiene having a known molecular weight was subjected to GPC measurement to determine a polystyrene conversion molecular weight of the standard polybutadiene, and from the polystyrene conversion molecular weight value X, a number average molecular weight of a soft segment block comprising a homopolymer of conjugated diene was calculated by employing conversion formula $Y = 0.58 \times X$ to be converted to absolute molecular weight value Y.

In the case of component B also, when number average molecular weight values of respective peaks corresponding to GPC chromatogram under measuring condition 1 of a mixture of S3 and S4 are represented respectively by M3 and M4 and number average molecular weight values of respective peaks corresponding to GPC chromatogram under

measuring condition 2 of a mixture of S3-B2 and S4-B2 are represented respectively by M7 and M8, value X obtained by the following formula is defined as a polystyrene conversion value of a number average molecular weight of a soft segment block.

$$X = \{(M7-M3) + (M8-M4)\}/2$$

Thereafter, a number average molecular weight of a soft segment block was calculated in the same manner as in Component A.

Each content of a branched block copolymer contained in component A and component B was determined by gel permeation chromatogram in the following manner.

In the case of component A, with regard to peaks corresponding to linear block copolymers S1-B1 and S2-B1 before coupling, peak top molecular weights M5 and M6 of components corresponding to S1-B1 and S2-B1 obtained from gel permeation chromatogram of sampling products after finishing third stage butadiene polymerization, were measured.

Thereafter, by selecting peaks of respective molecular weights M5 and M6 on gel permeation chromatogram of the component A finally obtained, peaks corresponding to S1-B1 and S2-B1 were determined.

Area of peaks of components corresponding to S1-B1 and S2-B1 thus determined, was calculated as an area of peak of a part enclosed by a base line and a perpendicular line drawn to the base line from a valley

between adjacent peaks.

A peak area of a branched block copolymer in component A was determined by calculating a sum of peak areas of these two components and deducting this value from the total chromatogram area value of component A. An area ratio by percentage of the peak area of branched block copolymer thus obtained to the total chromatogram area of component A was determined to be a branched block copolymer content in component A as mass%.

In the same manner as in component A, a branched block copolymer content in component B was determined by mass%.

A molar ratio of S1 and S2 in component A was determined in the following manner. In GPC chromatogram under measuring condition 1 of a mixture of S1 and S2, when peak top molecular weight values of respective peaks corresponding to components S1 and S2 are represented respectively by Mp1 and Mp2 and area ratios of respective peaks are represented respectively by A1 and A2, the molar ratio of S1 and S2 was calculated in accordance with the following formula.

S1:S2 (molar ratio) = (A1/Mp1):(A2/Mp2)

Also, in the same manner as in component A, a molar ratio of S3 and S4 in component B was determined.

A ratio of mol number of an opened epoxy group residue present in an epoxidized oil residue to a total mol number of the opened epoxy group residue and an epoxy

group present in the epoxidized oil residue in a block copolymer composition was determined in the following manner.

40 mg of a sample was dissolved in 1 ml of deuterium substituted chloroform, and proton NMR spectrum was measured by using JNM-α500FT-NMR manufactured by JEOL Ltd. under the following conditions.

Pulse width = 5.90 µs (45°), data point = 16384, repeating time = 7.0480 seconds, AD converter = 32 K bits, accumulated times = 792, sample tube = 5 mmΦ, and measuring temperature = room temperature

In the proton NMR spectrum thus obtained, a peak of methine proton (proton with ● mark in Fig. 1) derived from an epoxy group present in an epoxidized oil residue appears at 2.8 to 3.2 ppm. On the other hand, a peak of methine proton with ◎ mark in Fig. 2) derived from an opened epoxy group residue present in the epoxidized oil residue appears at 3.75 ppm.

By employing a chemical shift peak (area M) at 2.8 to 3.2 ppm and a chemical shift peak (area N) at 3.75 ppm, a ratio R of an opened epoxy group residue present in an epoxidized residue to a total mol number of the opened epoxy group residue and an epoxy group present in the epoxidized oil residue in the block copolymer composition was calculated in accordance with the following formula.

$$R = (2 \times N) / (M + 2 \times N)$$

Also, with regard to component A and component B, a ratio of a mol number of a ring-opened epoxy group residue present in an epoxidized oil residue to a total mol number of the ring-opened epoxy group residue and an epoxy group present in the epoxidized oil residue was determined by measuring proton NMR spectrum in the same manner as in the case of block copolymer composition.

EXAMPLE 1

First, component A was prepared in the following manner.

A stainless-made polymerization tank equipped with a jacket·stirrer and having an internal volume of 3 L was washed with cyclohexane and substituted with nitrogen, and then 1,233 g of cyclohexane dehydrated to a water content of at most 6 ppm and containing 150 ppm of tetrahydrofuran was charged into the polymerization tank, and 129 g of styrene dehydrated to a water content of at most 5 ppm was then added thereto. After raising an internal temperature to 50°C, 1.5 ml of a cyclohexane solution (mol concentration 1.2 mol/l) containing 10 mass% of n-butyl lithium was added thereto, and polymerization was effected for 20 minutes at such a temperature that the maximum temperature does not exceed 120°C (first stage polymerization).

Thereafter, under such a constant condition of an internal temperature of 50°C, 7.8 ml of a cyclohexane solution containing 10 mass% of n-butyl lithium and then

171 g of styrene dehydrated to a water content of at most 5 ppm were added and polymerized for 20 minutes at such a temperature that the maximum temperature does not exceed 120°C (second stage polymerization).

After finishing the second stage polymerization, sampling was made and a sampled polymerization solution was diluted with toluene, and the solution thus diluted was poured into a large amount of methanol to precipitate a polymer content which was then vacuum-dried to obtain a solid content. The solid content thus obtained was subjected to GPC measurement under measuring condition 1, and it was observed that two kinds of polystyrene chains were present in the sampled material, and when a material having a higher number average molecular weight is represented by M1 and a material having a lower number average molecular weight is represented by M2, the results were M1=95300 and M2=15700.

Further, after raising the internal temperature to 80°C, 111 g of butadiene dehydrated by passing through a molecular sieve was added, and the resultant material was polymerized for 20 minutes at such a temperature that the maximum temperature does not exceed 120°C (third stage polymerization).

After finishing the third stage polymerization, sampling was made, and the sampled polymerization solution was diluted with toluene, and the solution thus diluted was poured into a large amount of methanol to

precipitate a polymer content which was then vacuum-dried
to obtain a solid content. The solid content was then
subjected to GPC measurement under measuring condition 2,
and it was observed that two kinds of polymer chains

5   (styrene-butadiene diblock copolymers having respectively
different molecular weights) were present in the sampled
polymerization solution, and when a material having a
higher number average molecular weight (polystyrene
conversion value) is represented by M5 and a material

10   having a lower number average molecular weight is
represented by M6, the respective number average
molecular weights were M5=119500 and M6=36300.

After finishing the successive polymerization, a
solution having 1.4 g (corresponding to 1.3 equivalent)

15   of epoxidized soybean oil "Vikoflex 7170" (ATOFINA
CHEMICALS CO.) dissolved in 10 ml of cyclohexane was
added to the reaction solution under a constant condition
of an internal temperature of 80°C to carry out coupling
reaction for 30 minutes (coupling step).

20   The amount of epoxidized soybean oil "Vikoflex 7170"
added was determined in the following manner.

Since Vikoflex 7170 has a molecular weight of 1,000
and an oxirane oxygen content of 7.1%, Vikoflex 7170 has
4.4 mols of epoxy groups per mol. On the other hand,

25   since Vikoflex 7170 has 3 mols of carbonyl groups per
mol, Vikoflex 7170 has 10.4 mols of coupling reaction
sites per mol. Judging from the amount of n-butyl

lithium added at the first stage polymerization and the second stage polymerization, 0.0112 mol of lithium atom is calculated to be present in the reaction system. Thus, a mass amount of Vikoflex 7170 corresponding to 1.3 equivalents of lithium active terminals is calculated as illustrated below.

0.0112 (mol) × 1.3 (equivalent) × 1,000/10.4=1.4 g

Finally, all of polymerization-active terminals were deactivated with methanol to obtain a polymerization solution (polymer concentration 25 mass%) of component A.

After deactivation with methanol, sampling was made, and the sampled polymerization solution was diluted with toluene, and the solution thus diluted was poured into a large amount of methanol to precipitate a polymer content which was then vacuum-dried to obtain a solid content of component A.

Next, component B was prepared in the following manner.

After washing a stainless-made polymer tank equipped with a jacket·stirrer and having an internal volume of 3 L with cyclohexane and substituted with nitrogen, 1,222 g of cyclohexane dehydrated to a water content of at most 6 ppm and containing 150 ppm of tetrahydrofuran was charged into the polymerization tank under nitrogen gas atmosphere, and 189 g of styrene dehydrated to at most 5 ppm of water content was added thereto. After raising an internal temperature to 50°C, 1.5 ml of a cyclohexane

solution containing 10 mass% of n-butyl lithium was added thereto, and polymerization was effected for 20 minutes at such a temperature that the maximum temperature does not exceed 120°C (first stage polymerization).

5   Thereafter, under a constant condition of an internal temperature of 50°C, 10.0 ml of a cyclohexane solution containing 10 mass% of n-butyl lithium and then 76 g of styrene dehydrated to a water content of at most 5 ppm were added thereto, and polymerization was effected

10   for 20 minutes at such a temperature that the maximum temperature does not exceed 120°C (second stage polymerization).

After finishing the second stage polymerization, sampling was made and the sampled polymerization solution

15   was diluted with toluene, and the solution thus diluted was poured into a large amount of methanol to precipitate a polymer content which was then vacuum-dried to obtain a solid content. The solid content thus obtained was subjected to GPC measurement under measuring condition 1,

20   and it was found that two kinds of polystyrene chains were present in the sampled material, and when a material having a higher number average molecular weight is represented by M3 and a material having a lower number average molecular weight is represented by M4, the

25   respective number average molecular weights were M3=91100 and M4=6000.

Further, after raising the internal temperature to

80°C, 143 g of butadiene dehydrated by passing through a molecular sieve was added, and the polymerization was effected for 20 minutes at such a temperature that the maximum temperature does not exceed 120°C (third stage polymerization).

After finishing the third stage polymerization, sampling was made, and the sampled polymerization solution was diluted with toluene, and the solution thus diluted was poured into a large amount of methanol to precipitate a polymer content which was then vacuum-dried to obtain a solid content. The solid content thus obtained was subjected to GPC measurement under measuring condition 2, and it was observed that two kinds of polymer chains (styrene-butadiene diblock copolymers having respectively different molecular weights) were present in the sampled material, and when a material having a higher number average molecular weight (polystyrene conversion value) is represented by M7 and a material having a lower number average molecular weight is represented by M8, the respective number average molecular weights were M7=118400 and M8=26700.

After finishing the successive polymerization, a solution having 1.5 g (corresponding to 1.1 equivalents) of epoxidized soybean oil "Vikoflex 7170" (ATOFINA CHEMICALS CO.) dissolved in 10 ml of cyclohexane was added under a constant condition of an internal temperature of 80°C to carry out coupling reaction for 30

minutes (coupling step).

Finally, all of polymerization-active terminals were deactivated with methanol to obtain a polymerization solution (polymer concentration 25 mass%) of component B.

5   After deactivation with methanol, sampling was made, and the sampled polymerization solution was diluted with toluene, and the solution thus diluted was poured into a large amount of methanol to precipitate a polymer content which was then vacuum-dried to obtain a solid content of

10   component B. Thereafter, 1,300 g of each of polymerization solutions of component A and component B was weighed respectively in an equal amount, and the two polymerization solutions were fully mixed. The polymerization solutions thus mixed were diluted with

15   cyclohexane, and the solution thus mixed was poured into a large amount of methanol to precipitate a polymer content which was then vacuum-dried to obtain a powdery polymer.

Finally, after adding 0.2 mass part of 2,4-

20   bis[(octylthio)methyl]-o-cresol as a stabilizer to 100 mass parts of the powdery polymer, the powdery polymer was charged into a 20 mm monoaxial extruder, and a melt strand was withdrawn from a dice at 210°C, and was cooled with water, and was then cut by a cutter to obtain

25   pellet-like resin (block copolymer composition). Respective charged amounts are shown in Tables 1 and 5, and respective analyzed values are shown in Tables 2 to 4

and Tables 6 to 9, and evaluation results of solid

physical properties are shown in Table 10.

EXAMPLES 2 to 9 and COMPARATIVE EXAMPLES 1 to 8

Component A and component B were prepared and they

5   were mixed to obtain pellet-like block copolymer

composition in the same manner as in Example 1, except

that polymerization tanks having such volumes and such

charged amounts of starting materials as shown in Tables

1, 5, 12 and 16 were employed in Examples 2 to 9 and

10   Comparative Examples 1 to 8. Various analytical values

are shown in Tables 2 to 4, Tables 6 to 9, Tables 13 to

15 and Tables 17 to 20, and evaluation results of solid

physical properties are shown in Tables 10 and 21.

GPC measurement after finishing the second stage

15   polymerization was made under measuring condition 1, and

GPC measurement after finishing the third stage

polymerization was made under measuring condition 2, and

the obtained component A, component B and block copolymer

composition were subjected to gel permeation chromatogram

20   measurement under measuring condition 2.

EXAMPLES 10 to 18 and COMPARATIVE EXAMPLES 9 to 16

The block copolymer compositions obtained in

Examples 1 to 9 and Comparative Examples 1 to 8 were

respectively blended with general-purpose polystyrene

25   (G14L manufactured by TOYO-STYRENE CO., LTD.) in such

weight ratios of block copolymer composition/general-

purpose polystyrene as shown in Tables 11 and 22, and

each of the blended materials was charged into a 20 mm

monoaxial extruder and melt strands were withdrawn from a

dice at 230°C, and were cooled with water and were cut by

a cutter to obtain pellet-like resin. Thereafter, their

5 physical properties were evaluated in the same manner as

in Example 1, and the results are shown in Tables 11 and

22.

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TABLE 1

Charge amounts of component A

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Volume of polymerization tank (L)	3	3	3	3	3	10	3	10	10
Solvent cyclohexane (g)	1233	1225	1225	1166	1188	3952	1224	3950	3950
Solvent/total monomer amount (wt ratio)	3.0	3.0	3.0	2.3	2.6	2.6	3.0	2.6	2.6
First stage n-BuLi 10% cyclohexane solution (ml)	1.5	1.1	1.2	2.3	1.4	6.5	0.6	4.9	6.3
First stage styrene (g)	129	121	121	264	184	739	59	573	730
Second stage n-BuLi 10% cyclohexane solution (ml)	7.8	7.2	8.1	5.7	6.3	15.8	11.7	16.3	16
Second stage styrene (g)	171	161	161	146	161	409	212	574	417
Butadiene (g)	111	127	127	90	117	389	136	389	389
Vikoflex7170(g)	1.4	1.3	1.3	1.0	1	3.6	1.7	3.7	3.6
Equivalent number of Vikoflex7170	1.3	1.4	1.2	1.1	1.1	1.4	1.2	1.5	1.4

TABLE 2

Analytical values of polymer content in component A produced by second stage polymerization

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
GPC measuring condition of polymer content obtained after finishing second stage polymerization	1	1	1	1	1	1	1	1	1
Number average molecular weight M1 of component S1 in polymer content obtained after finishing second stage polymerization (M1>M2)	95300	85200	90100	136200	119200	149000	77300	145300	158100
Number average molecular weight M2 of component S2 in polymer content obtained after finishing second stage polymerization (M1>M2)	15700	15600	16200	17100	18200	19500	16000	26000	20000
Ratio M1/M2	6.1	5.5	5.6	8.0	6.5	7.6	4.8	5.6	7.9
Molar ratio of component S1 providing number average molecular weight M1 in polymer content obtained after finishing second stage polymerization (M1>M2)	15	17	16	29	20	27	7	21	24
Molar ratio of component S2 providing number average molecular weight M2 in polymer content obtained after finishing second stage polymerization (M1>M2)	85	83	84	71	80	73	93	79	76

TABLE 3

Analytical values of polymer content in component A produced by third stage polymerization

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
GPC measuring condition of polymer content obtained after finishing third stage polymerization	2	2	2	2	2	2	2	2	2
Number average molecular weight $M5$ of component $S1$-$B1$ in polymer content obtained after finishing third stage polymerization ($M5>M6$)	119500	114400	122000	161500	153200	199400	103300	192700	209800
Number average molecular weight $M6$ of component $S2$-$B1$ in polymer content obtained after finishing third stage polymerization ($M5>M6$)	36300	40600	42700	39700	45900	57700	37800	62500	56400
Number average molecular weight of polymer block $B1$ prepared from a conjugated diene as a monomer	12992	15718	16936	13891	17893	25694	13862	24331	25549

TABLE 4

Analytical values of component A

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
GPC measuring condition of obtained component A	2	2	2	2	2	2	2	2	2
Weight average molecular weight by GPC of obtained component A	125300	131200	135200	196800	175300	218300	96800	196800	219000
Number average molecular weight by GPC of obtained component A	88800	94300	98100	131100	115800	154800	77500	138500	147000
Molecular weight distribution by GPC of obtained component A	1.41	1.39	1.38	1.50	1.51	1.41	1.25	1.42	1.49
Content (%) of branched block copolymer component in component A	80	71	71	83	79	77	65	70	76
Ratio of mol number of ring-opened epoxy group residue present in epoxidized oil residue to total mol number of epoxy group and ring-opened epoxy group residue measured by NMR	0.10	0.12	0.11	0.14	0.15	0.09	0.11	0.09	0.09
PBd amount (%)	27	31	31	18	25	25	33	25	25
Polymer concentration (mass%) in polymerization solution of component A	25	25	25	30	28	28	25	28	28

TABLE 5

Charge amounts of component B

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Volume of polymerization tank (L)	3	3	3	3	10	3	10	3	3
Solvent cyclohexane (g)	1222	1228	1228	1141	3952	1186	4094	1185	1183
Solvent/total monomer amount (wt ratio)	3.0	3.0	3.0	2.3	2.6	2.6	3.0	2.6	2.6
First stage n-BuLi 10% cyclohexane solution (ml)	1.5	1.6	1.8	1.7	5.8	1.7	6.8	1.4	1.7
First stage styrene (g)	189	202	202	206	807	216	740	194	235
Second stage n-BuLi 10% cyclohexane solution (ml)	10	10.4	11.8	12.6	29.2	13.2	29.9	14.4	12.4
Second stage styrene (g)	76	81	81	123	341	129	218	150	108
Butadiene (g)	143	127	127	160	389	117	407	117	116
Vikoflex7170 (g)	1.5	1.9	1.6	1.7	4.7	2.4	5.1	2.8	2.5
Equivalent number of Vikoflex7170	1.1	1.4	1.0	1.0	1.2	1.4	1.2	1.5	1.5

TABLE 6

Analytical values of polymer content in component B produced by second stage polymerization

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
GPC measuring condition of polymer content obtained after finishing second stage polymerization	1	1	1	1	1	1	1	1	1
Number average molecular weight M3 of component S3 in polymer content obtained after finishing second stage polymerization (M3>M4)	91100	93200	123800	102300	138100	126600	111500	123400	150400
Number average molecular weight M4 of component S4 in polymer content obtained after finishing second stage polymerization (M3>M4)	6000	5400	6000	7400	8800	8200	5900	8300	6900
Ratio M3/M4	15.2	17.3	20.6	13.8	15.7	15.4	18.9	14.9	21.8
Molar ratio of component S3 providing number average molecular weight M3 in polymer content obtained after finishing second stage polymerization (M3>M4)	21	17	13	13	16	12	19	10	11
Molar ratio of component S4 providing number average molecular weight M4 in polymer content obtained after finishing second stage polymerization (M3>M4)	79	83	87	87	84	88	81	90	89

TABLE 7

Analytical values of polymer content in component B produced by third stage polymerization

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
GPC measuring condition of polymer content obtained after finishing third stage polymerization	2	2	2	2	2	2	2	2	2
Number average molecular weight M7 of component S3–B2 in polymer content obtained after finishing third stage polymerization (M7>M8)	118400	119800	152300	131500	170400	154200	142600	140600	178400
Number average molecular weight M8 of component S4–B2 in polymer content obtained after finishing third stage polymerization (M7>M8)	26700	24300	25100	27800	29700	25400	28400	22700	23100
Number average molecular weight of polymer block B2 prepared from a conjugated diene as a monomer	13920	13195	13804	14384	15428	12992	15544	9164	12818

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TABLE 8

Analytical values of component B

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
GPC measuring condition of obtained component B	2	2	2	2	2	2	2	2	2
Weight average molecular weight by GPC of obtained component B	140100	127100	148200	139800	177500	135900	158500	113600	157000
Number average molecular weight by GPC of obtained component B	93600	81300	86500	89600	109000	79100	102100	63100	80700
Molecular weight distribution by GPC of obtained component B	1.50	1.56	1.71	1.56	1.63	1.72	1.55	1.80	1.95
Content (%) of branched block copolymer component in component B	85	83	85	82	81	79	82	78	86
Ratio of mol number of ring-opened epoxy group residue present in epoxidized oil residue to total mol number of epoxy group and ring-opened epoxy group residue measured by NMR	0.14	0.11	0.15	0.14	0.14	0.10	0.11	0.10	0.11
PBd amount (%)	35	31	31	33	25.3	25.3	29.8	25.3	25.3
Polymer concentration (mass%) in polymerization solution of component B	25	25	25	30	28	28	25	28	28

TABLE 9

Analytical values of obtained block copolymer mixture

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Mass (g) of mixed polymerization solution of component A	1300	1300	1300	1300	1300	1300	1300	1300	1300
Mass (g) of mixed polymerization solution of component B	1300	1300	1300	1300	2600	1300	2600	1300	1300
Mass ratio of component A/component B	1/1	1/1	1/1	1/1	1/2	1/1	1/2	1/1	1/1
GPC measuring condition of obtained block copolymer mixture	2	2	2	2	2	2	2	2	2
Weight average molecular weight by GPC of obtained block copolymer mixture	127000	128600	146800	172000	180300	177000	136300	156800	187100
Number average molecular weight by GPC of obtained block copolymer mixture	84500	85700	93100	108900	114700	104500	88200	89400	103800
Molecular weight distribution by GPC of obtained block copolymer mixture	1.50	1.50	1.58	1.58	1.57	1.69	1.55	1.75	1.80
Ratio of mol number of ring-opened epoxy group residue present in epoxidized oil residue to total mol number of epoxy group and ring-opened epoxy group residue measured by NMR	0.12	0.11	0.13	0.14	0.14	0.10	0.11	0.10	0.10
PBd amount (%)	31	31	31	25	25	25	31	25	25

TABLE 10

Measurement results of physical properties of block copolymer mixture

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
MFR (g/10 min)	9.3	9.5	6.6	4.1	2.8	2.5	8.7	4.3	2
Cloudiness (%)	1.8	1.8	1.9	1.5	1.3	1.4	1.8	1.3	1.6
Total light transmittance (%)	89.3	89.2	89	90	91	90	89.1	91	89
Total absorption energy (J)	13	12	13.5	12.5	13.4	11.7	15	11.5	15.4
Charpy impact strength (kJ/m)	6.5	6	6.7	5.7	6.3	5.1	7.7	6.1	9.8

TABLE 11

Measurement results of physical properties of blended products of block copolymer mixture and general-purpose polystyrene

	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18
Kinds of used block copolymer mixture	Polymer of Ex. 1	Polymer of Ex. 2	Polymer of Ex. 3	Polymer of Ex. 4	Polymer of Ex. 5	Polymer of Ex. 6	Polymer of Ex. 7	Polymer of Ex. 8	Polymer of Ex. 9
Mass ratio of block copolymer mixture/general-purpose polystyrene	60/40	60/40	60/40	80/20	80/20	80/20	60/40	80/20	80/20
MFR (g/10 min)	7.2	7.8	6.2	4.2	3.3	3.1	7.5	4.8	2.8
Haze (%)	7.1	7	8	3.8	2.9	3.8	8	2.4	4
Total light transmittance (%)	82	81.7	81	86.1	87.5	86.8	80.2	88	86.3
Total absorption energy (J)	11.1	7.5	11.2	2.5	3.5	3.2	12.1	3	12.8
Charpy impact strength (kJ/m)	1.4	1.3	1.5	1.3	1.3	1.3	1.4	1.3	1.4

TABLE 12

Charge amounts of component A

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Volume of polymerization tank (L)	3	3	3	3	3	3	3	3
Solvent cyclohexane (g)	1227	1166	1163	1237	1229	1228	1225	1227
Solvent/total monomer amount (wt ratio)	3.0	2.3	2.3	3.0	3.0	3.0	3.0	3.0
First stage n–BuLi 10% cyclohexane solution (ml)	1.5	0.7	1.3	0.9	2.3	1.3	2.3	0.8
First stage styrene (g)	135	78	194	141	132	143	191	39
Second stage n–BuLi 10% cyclohexane solution (ml)	6.2	6.1	7.5	6.1	10.7	7	2.7	11.7
Second stage styrene (g)	147	336	206	187	150	139	90	243
Butadiene (g)	127	86	99	85	127	127	127	127
Vikoflex7170(g)	1.0	0.8	1.1	1.0	1.7	2.6	0.3	1.6
Equivalent number of Vikoflex7170	1.1	1.0	1.1	1.2	1	3	1	1

TABLE 13

Analytical values of polymer content in component A produced by second stage polymerization

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
GPC measuring condition of polymer content obtained after finishing second stage polymerization	1	1	1	1	1	1	1	1
Number average molecular weight M1 of component S1 in polymer content obtained after finishing second stage polymerization (M1>M2)	86400	147300	172500	144600	61000	152000	95000	96000
Number average molecular weight M2 of component S2 in polymer content obtained after finishing second stage polymerization (M1>M2)	15300	53400	21600	24500	10000	15100	17300	17500
Ratio M1/M2	5.6	2.8	8.0	5.9	6.1	10.1	5.5	5.5
Molar ratio of component S1 providing number average molecular weight M1 in polymer content obtained after finishing second stage polymerization (M1>M2)	21	11	13	14	15	10	41	3
Molar ratio of component S2 providing number average molecular weight M2 in polymer content obtained after finishing second stage polymerization (M1>M2)	79	89	87	86	85	90	59	97

TABLE 14

Analytical values of polymer content in component A produced by third stage

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
GPC measuring condition of polymer content obtained after finishing third stage polymerization	2	2	2	2	2	2	2	2
Number average molecular weight M5 of component S1–B1 in polymer content obtained after finishing third stage polymerization (M5>M6)	117400	193000	210500	180200	86500	202000	151000	129000
Number average molecular weight M6 of component S2–B1 in polymer content obtained after finishing third stage polymerization (M5>M6)	43200	82000	44300	46300	25500	39800	59200	33000
Number average molecular weight of polymer block B1 prepared from a conjugated diene as a monomer	17081	21547	17603	16646	11890	21663	28391	14065

TABLE 15

Analytical values of component A

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
GPC measuring condition of obtained component A	2	2	2	2	2	2	2	2
Weight average molecular weight by GPC of obtained component A	162000	205600	193700	171600	153000	173000	173000	159000
Number average molecular weight by GPC of obtained component A	121300	153600	124100	118200	108000	123000	110300	129000
Molecular weight distribution by GPC of obtained component A	1.34	1.34	1.56	1.45	1.42	1.41	1.57	1.23
Content (%) of branched block copolymer component in component A	73	82	81	78	75	77	70	74
Ratio of mol number of ring-opened epoxy group residue present in epoxidized oil residue to total mol number of epoxy group and ring-opened epoxy group residue measured by NMR	0.14	0.14	0.15	0.10	0.14	0.02	0.85	0.14
PBd amount (%)	31	17	20	21	31	31	31	31
Polymer concentration (mass%) in polymerization solution of component A	25	30	30	25	25	25	25	25

TABLE 16

Charge amounts of component B

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Volume of polymerization tank (L)	3	3	3	3	3	3	3	3
Solvent cyclohexane (g)	1227	1152	1155	1228	1225	1227	1226	1229
Solvent/total monomer amount (wt ratio)	3.0	2.3	2.3	3.0	3.0	3.0	3.0	3.0
First stage n-BuLi 10% cyclohexane solution (ml)	1.5	1.6	1.8	1.3	2.8	1.4	2.5	1.1
First stage styrene (g)	147	253	240	212	218	147	235	77
Second stage n-BuLi 10% cyclohexane solution (ml)	14	8	10	8	15.3	15	3	20.8
Second stage styrene (g)	135	119	126	85	63	135	47	205
Butadiene (g)	127	122	129	112	127	127	127	127
Vikoflex7170(g)	1.9	1.2	1.4	1.1	2.3	5.1	0.4	2.8
Equivalent number of Vikoflex7170	1.1	1.1	1.0	1.0	1.1	2.7	0.6	1.1

TABLE 17

Analytical values of polymer content in component B produced by second stage polymerization

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
GPC measuring condition of polymer content obtained after finishing second stage polymerization	1	1	1	1	1	1	1	1
Number average molecular weight M3 of component S3 in polymer content obtained after finishing second stage polymerization (M3>M4)	102800	169200	148000	162200	71500	111000	111100	102000
Number average molecular weight M4 of component S4 in polymer content obtained after finishing second stage polymerization (M3>M4)	8800	12200	9800	8800	3100	8300	8400	9100
Ratio M3/M4	11.7	13.9	15.1	18.4	23.1	13.4	13.2	11.2
Molar ratio of component S3 providing number average molecular weight M3 in polymer content obtained after finishing second stage polymerization (M3>M4)	12	15	12	13	13	11	40	3
Molar ratio of component S4 providing number average molecular weight M4 in polymer content obtained after finishing second stage polymerization (M3>M4)	88	85	88	87	87	89	60	97

TABLE 18

Analytical values of polymer content in component B produced by third stage polymerization

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
GPC measuring condition of polymer content obtained after finishing third stage polymerization	2	2	2	2	2	2	2	2
Number average molecular weight M7 of component S3-B2 in polymer content obtained after finishing third stage polymerization (M7>M8)	126600	210900	184500	196800	84500	129500	148000	119200
Number average molecular weight M8 of component S4-B2 in polymer content obtained after finishing third stage polymerization (M7>M8)	25000	38400	31600	32300	14500	24700	45900	17500
Number average molecular weight of polymer block B2 prepared from a conjugated diene as a monomer	11600	19691	16907	16849	7076	10121	21576	7424

TABLE 19

Analytical values of component B

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
GPC measuring condition of obtained component B	2	2	2	2	2	2	2	2
Weight average molecular weight by GPC of obtained component B	114700	219200	183500	200300	108000	113000	115000	121000
Number average molecular weight by GPC of obtained component B	74300	130400	108800	114200	65000	73300	67000	89000
Molecular weight distribution by GPC of obtained component B	1.54	1.68	1.69	1.75	1.66	1.54	1.72	1.36
Content (%) of branched block copolymer component in component B	85	81	81	81	82	84	77	83
Ratio of mol number of ring-opened epoxy group residue present in epoxidized oil residue to total mol number of epoxy group and ring-opened epoxy group residue measured by NMR	0.14	0.15	0.14	0.14	0.14	0.02	0.9	0.14
PBd amount (%)	31	25	26	27	31	31	31	31
Polymer concentration (mass%) in polymerization solution of component B	25	30	30	25	25	25	25	25

TABLE 20

Analytical values of obtained block copolymer mixture

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Mass (g) of mixed polymerization solution of component A	1300	1300	1300	1300	1300	1300	1300	1300
Mass (g) of mixed polymerization solution of component A	1300	1300	1300	1300	1300	1300	1300	1300
Mass ratio of component A/component B	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1
GPC measuring condition of obtained block copolymer mixture	2	2	2	2	2	2	2	2
Weight average molecular weight by GPC of obtained block copolymer mixture	139800	207900	192300	186100	125000	147000	141000	140500
Number average molecular weight by GPC of obtained block copolymer	92100	123300	115600	119500	83500	96500	84500	115000
Molecular weight distribution by GPC of obtained block copolymer mixture	1.52	1.69	1.66	1.56	1.50	1.52	1.67	1.22
Ratio of mol number of ring-opened epoxy group residue present in epoxidized oil residue to total mol number of epoxy group and ring-opened epoxy group residue measured by NMR	0.15	0.14	0.14	0.12	0.14	0.02	0.87	0.14
PBd amount (%)	31	21	23	24	31	31	31	31

Table 21

Measurement results of physical properties of block copolymer

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
MFR (g/10 min)	7.6	1	2.2	1.8	13	5.5	9.5	7.4
Haze (%)	1.5	2.1	1.5	1.9	1.4	1.8	1.8	1.3
Total light transmittance (%)	89.3	89.9	90.8	88.9	89.7	88.7	89	89.9
Total absorption energy (J)	3	2	3	2	1	0.9	0.8	0.5
Charpy impact strength (kJ/m)	1	0.8	1.1	1.1	0.5	0.7	0.6	0.5

TABLE 22

Measurement results of physical properties of blended products of block copolymer mixture and general-purpose polystyrene

	Comp. Ex. 9	Comp. Ex. 10	Comp. Ex. 11	Comp. Ex. 12	Comp. Ex. 13	Comp. Ex. 14	Comp. Ex. 15	Comp. Ex. 16
Kinds of used block copolymer mixture	Polymer of Comp. Ex. 1	Polymer of Comp. Ex. 2	Polymer of Comp. Ex. 3	Polymer of Comp. Ex. 4	Polymer of Comp. Ex. 5	Polymer of Comp. Ex. 6	Polymer of Comp. Ex. 7	Polymer of Comp. Ex. 8
Mass ratio of block copolymer mixture/general-purpose polystyrene	60/40	80/20	80/20	80/20	60/40	60/40	60/40	60/40
MFR (g/10 min)	7.1	1.5	2.8	2.2	11	6.9	8.1	7.2
Haze (%)	6.8	4.9	3.8	6.5	7.5	8.5	9.9	6.9
Total light transmittance (%)	81.8	88.2	86.1	85.6	80.2	78.9	78.2	81.2
Total absorption energy (J)	1.7	0.7	1	1	0.7	0.8	0.7	0.4
Charpy impact strength (kJ/m)	1.3	1.5	1.1	1.3	0.4	0.7	0.7	0.5

INDUSTRIAL APPLICABILITY

The block copolymer composition of the present invention is useful as modifiers for various thermoplastic resins and thermosetting resins, base materials for shoes, base materials for self-adhesives·adhesives, modifiers for asphalt, modifiers for electric wire cables, modifiers for vulcanized rubbers and the like, to which conventional block copolymers have been applicable.

Particularly, a composition prepared by blending the block copolymer composition of the present invention with various thermoplastic resins is useful as a base material for a sheet and a film, and is effectively usable as wrapping materials or containers for foods and daily goods, and also as laminate sheet·films, which are excellent in transparency, impact resistance and low temperature properties.